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| <b>(54) Title:</b> NICKEL BASED ALLOY FOR REPAIRING SUBSTRATES   |           |  |
| <b>(57) Abstract</b><br><br>A nickel-based polycrystalline alloy comprising 0.03-1.9 % hafnium, 0.003-0.32 % boron, 0.02-0.16 % yttrium and 0.007-0.35 % zirconium is disclosed. A method of repairing nickel-based superalloy substrates using the above-described alloy is also disclosed. The present invention further provides a method for the repair of single crystal alloy substrates by the application of a repair alloy wherein the repair alloy's composition is similar to or the same as the single crystal alloy composition except that the repair alloy additionally comprises grain boundary strengtheners and/or oxidation resistance enhancers.   |           |  |

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## NICKEL BASED ALLOY FOR REPAIRING SUBSTRATES.

FIELD OF THE INVENTION

5 This invention relates to a method for the repair of nickel-based equiaxed, directionally solidified, and single crystal superalloys. The present invention also provides polycrystalline nickel-based alloys comprising 0.03 to 2.5 weight % hafnium, 0.003 to 0.32 weight % boron, 0.02 to 0.16 weight % yttrium, and 0.007 to 0.35 weight % zirconium, and the use of these alloys in the  
10 repair of equiaxed, directionally solidified, and single crystal nickel-based alloy substrates, such as airfoils.

The present invention further provides a repair alloy and a method for the repair of single crystal  
15 superalloys.

BACKGROUND OF THE INVENTION

Nickel-based superalloys have found use in a variety of high technology applications. Single crystal, directionally solidified and equiaxed nickel-based alloys that exhibit strength and oxidation  
20 resistance at high temperature are particularly useful in forming engine components. Examples of single crystal nickel-based superalloys can be found in U.S. Patent Nos. 4,849,030 (Darolia et al.), 4,719,080 (Duhl

et al.) and 5,151,249 (Austin et al.). Other examples of nickel-based alloys are disclosed in U.S. Patent Nos. 3,832,167 (Shaw et al.), 4,983,233 (Henry), 5,171,380 (Henry), and U.S. Patent Application Serial No. 5 07/944,184 (Gostic et al.). All references cited herein are incorporated by reference as if reproduced in full below.

Since articles composed of nickel-based superalloys are often expensive or difficult to replace, there is a  
10 need for methods of preventing damage to or repairing such articles, especially articles composed of single crystal nickel-based superalloys. In an effort to prevent damage to the underlying substrates, various protective coatings have been applied to the surface of  
15 articles formed of nickel-based superalloys. See e.g., U.S. Patent Nos. 4,054,723 (Higginbotham et al.), 4,743,514 (Strangman et al.), and 5,043,138 (Darolia et al.). U.S. Patent No. 4,830,934 (Ferrigno et al.) discloses a method for the repair of multi-crystalline  
20 nickel-based superalloys using a nickel-based repair alloy. A method for the repair of articles formed from superalloys which repairs a damaged alloy substrate by brazing onto the damaged substrate a mixture of a transient liquid phase (TLP) alloy and a higher melting  
25 alloy is described in U.S. Patent Nos. 4,008,844 and 4,073,639 (Duvall et al.).

Despite prior efforts in the areas of coatings on nickel-based substrate alloys and repair of nickel-based

superalloys, there remains a need for new methods of repairing nickel-based superalloy substrates, especially single crystal nickel-based superalloy substrates. There is a corresponding need for a nickel-based alloy  
5 that is suitable for the coating or repair of substrates. These needs are exacerbated by the increasing operating temperatures of modern and developing engines and the accompanying increased rate of erosion of engine components. Build-up of the eroded  
10 areas is required for continued operation, to provide recontour to original performance configurations and to create an erosion barrier to protect the underlying remaining substrate.

#### SUMMARY OF THE INVENTION

15 The present invention provides a method for the repair of nickel-based superalloy substrates by the application of a repair alloy wherein the repair alloy's composition is similar to or the same as the nickel-based superalloy composition except that the repair  
20 alloy additionally controls the specific levels of elemental grain boundary strengtheners and/or oxidation resistance enhancers. The present invention also provides a method for the repair of single crystal alloy substrates by the application of a repair alloy wherein  
25 the repair alloy's composition is similar to or the same as the single crystal alloy composition except that the

repair alloy additionally comprises grain boundary strengtheners and/or oxidation resistance enhancers.

5 In the present invention, repair alloys deposited onto a superalloy substrate should exhibit good bonding and a good thermal expansion match with the substrate. For these reasons, it is desirable that the repair alloy have a composition that is similar to the composition of the substrate alloy. Because current application techniques produce a polycrystalline repair alloy, it is 10 also important to the present invention that the repair alloy contain grain boundary strengtheners. Grain boundary strengthening elements are known in the metallurgical arts, and may vary depending upon the composition of the matrix alloy. During casting and 15 subsequent heat treatment, grain boundary strengtheners tend to diffuse into grain boundaries in the microstructure of an alloy, resulting in enhanced creep and rupture ductility. In cases in which the repair alloy is applied to a single crystal or directionally 20 solidified substrate article the requisite grain boundary strengthening elements may not be available from the substrate metal for diffusion into the applied repair alloy. Therefore, in these instances, it is important to provide grain boundary strengthening 25 elements in the repair alloys of the present invention. In the case where the substrate alloy is a polycrystalline nickel-based superalloy, the repair alloy typically does not require additional amounts of

grain boundary strengtheners since the grain boundary strengtheners are generally already present in the polycrystalline substrate alloy. In nickel-based repair alloys of the present invention, boron, hafnium and zirconium are utilized as grain boundary strengtheners.

It is also important that the repair alloys of the present invention have excellent oxidation resistance. Thus, it is desirable to add one or more elements that enhance oxidation resistance. Elements that enhance oxidation resistance in alloys are known in the metallurgical arts, and may vary depending upon the composition of the matrix alloy. Yttrium, and the rare earth elements can be added to enhance oxidation resistance. In the present invention, yttrium is used to enhance the oxidation resistance of a nickel-based repair alloy.

Grain boundary strengthening elements can reduce oxidation resistance. In the repair alloys of the present invention, levels of particular elements, especially boron, hafnium, zirconium and yttrium, are controlled to maximize high temperature capability and oxidation resistance.

The build-up repair alloys of the present invention are applied by low substrate heat input build-up processes including: laser welding, plasma transfer arc welding and low pressure plasma spray.

Repair methods of the present invention offer many advantages over conventional brazing repairs. The

above-described low substrate heat input build-up repair processes melt the repair alloy prior to application to the substrate, thus significantly reducing heating of the substrate alloy and thereby reducing the possibilities of heat-altered zone cracking and overall recrystallization of the repair article. Avoiding overall recrystallization is especially advantageous in single crystal repair applications where substrate recrystallization property debit concerns limit the upper bounds of thermal processing.

Brazing repair forces thermal treatment of the entire repair article. In contrast, the methods of the present invention allow repair of the damaged area while the critical property regions (e.g., high stress attachment features of turbine blades and vanes) avoid exposure to high temperature.

Repair alloys for brazing applications require substantial amounts of boron and/or silicon to depress the melting points of the alloys. The repair methods of the present invention do not require the repair alloys to have substantially lower melting temperatures than the substrates and thus, far less boron and/or silicon is required in the repair alloys of the present invention. As a result, oxidation resistance has been significantly improved. Also, the repair methods of the present invention enable the composition of the repair alloys of the present invention to be adjusted to more closely match the compositions of the substrate alloys.



The present invention provides a method of creating a build-up alloy application on a single crystal superalloy substrate. In this method a repair alloy is formulated to contain substantially the same elements in substantially the same proportions as in the single crystal substrate except that the repair alloy additionally contains a grain boundary strengthener element or elements; and the repair alloy is applied to the single crystal substrate by a low substrate heat input buildup process. In another preferred embodiment of this method, the repair alloy additionally contains an element that enhances oxidation resistance preferably yttrium. It is preferred that the levels of additional grain boundary strengtheners are insufficient to substantially reduce the bulk melting point of the repair alloy (i.e. substantially less boron than is used to depress the melting point of repair alloys in brazing techniques).

The present invention also provides a polycrystalline nickel-based alloy comprising 0.03 to 2.5 weight % hafnium, 0.003 to 0.32 weight % boron, 0.007 to 0.35 weight % zirconium, and 0.02 to 0.16 weight % yttrium. (Unless otherwise indicated, all percentages and parts per million (ppm) set forth herein are weight percentages.) This combination of elements results in particularly desirable characteristics of nickel-based alloys for build-up applications.

It is particularly important to control the levels of yttrium in the nickel-based repair alloys of the present invention, levels of yttrium less than about 0.02% do not impart a sufficient degree of oxidation resistance. Levels of yttrium substantially in excess of about 0.16% do not improve oxidation resistance and may, depending on various factors such as intended application and thermal processing, introduce undesirable characteristics such as precipitation of yttride phases and changes in melting properties.

Within the above-described ranges of hafnium, boron, zirconium, and yttrium, it is desirable that the composition of the nickel-based repair alloy of the present invention be selected to correspond to the composition of the substrate alloy. In a preferred embodiment, shown in the table below, the composition ranges, by percent, of two nickel-based single crystal substrates and the composition range of a repair alloy for the repair of nickel-based single crystal substrates are:

TABLE 1

|    | substrate alloy |    |       | substrate alloy | repair alloy |
|----|-----------------|----|-------|-----------------|--------------|
| Cr | 9.5             | -  | 10.5  | 4.75 - 5.25     | 4.75 - 10.5  |
| Al | 4.75            | -  | 5.25  | 5.5 - 5.8       | 4.75 - 5.8   |
| W  | 3.75            | -  | 4.25  | 5.6 - 6.2       | 3.75 - 6.2   |
| Ta | 11.75           | -  | 12.25 | 8.4 - 9.0       | 8.4 - 12.25  |
| Mo |                 | -- |       | 1.7 - 2.1       | 0 - 2.1      |
| Co | 4.5             | -  | 5.5   | 9.5 - 10.5      | 4.5 - 10.5   |

|    |        |                          |                          |                          |
|----|--------|--------------------------|--------------------------|--------------------------|
|    | Ti     | 1.25 - 1.75              | --                       | 0 - 1.75                 |
|    | Cb(Nb) | --                       | --                       | --                       |
|    | Re     | --                       | 2.8 - 3.2                | 0 - 3.2                  |
|    | C      | 0.050                    | 0.050                    | 0.05 - .17               |
| 5  | B      | 0.0030                   | 0.0030                   | 0.003-0.32               |
|    | Zr     | 0.0075                   | 0.0075                   | 0.007-0.15               |
|    | Y      | --                       | --                       | 0.2 - 0.16               |
|    | Hf     | 0.0030                   | 0.05 - 0.15              | 0.03 - 1.9               |
| 10 | Ni     | essentially<br>remainder | essentially<br>remainder | essentially<br>remainder |

In another preferred embodiment, shown in the following table, percent composition ranges of two directionally solidified (i.e. columnar) nickel-based superalloy substrates and the composition range of a repair alloy for the repair of directionally solidified nickel-based superalloy substrates are:

| <u>TABLE 2</u> |                    |                 |              |
|----------------|--------------------|-----------------|--------------|
|                | substrate alloy    | substrate alloy | repair alloy |
|                | Cr 8-10            | 6.0 - 6.8       | 6.0 - 10.00  |
| 20             | Al 4.75 - 5.25     | 5.7 - 6.1       | 4.75 - 6.1   |
|                | W 11.5 - 12.5      | 6.0 - 6.8       | 6.0 - 12.5   |
|                | Ta --              | 3.75- 4.25      | 0 - 4.25     |
|                | Mo --              | 1.5 - 1.9       | 0 - 1.9      |
|                | Co 9.25 - 11.0     | 12.1-13.0       | 9.25 - 13.0  |
| 25             | Ti 1.75 - 2.25     | --              | 0 - 2.25     |
|                | Cb(Nb) 0.75 - 1.25 | --              | 0 - 1.25     |
|                | Re --              | 2.75 -3.25      | 0 - 3.25     |

|   |    |                          |                          |                          |
|---|----|--------------------------|--------------------------|--------------------------|
|   | C  | 0.12 - 0.16              | 0.08 - 0.12              | 0.08 - 0.16              |
|   | B  | 0.010 - 0.020            | 0.010-0.015              | 0.003-0.020              |
|   | Zr | 0.120                    | 0.04- 0.12               | 0.04 - 0.12              |
|   | Y  | --                       | --                       | 0.02 - 0.16              |
| 5 | Hf | 1.50 - 2.50              | 1.0 - 2.0                | 1.0 - 2.5                |
|   | Ni | essentially<br>remainder | essentially<br>remainder | essentially<br>remainder |

10 In another preferred embodiment, shown in the table below, percent composition ranges of four equiaxed substrate alloys and the composition range of a repair alloy for the repair of equiaxed alloys are:

TABLE 3

|    |        | substrate<br>alloy       | substrate<br>alloy       | substrate<br>alloy       | substrate<br>alloy       | repair<br>alloy          |
|----|--------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 5  | Cr     | 7.5 - 8.5                | 8.0 - 8.8                | 9.5 - 10.5               | 8.0 - 11.0               | 7.5 - 11.0               |
|    | Al     | 5.75 - 6.25              | 5.3 - 5.7                | 6.5 - 6.7                | 5.0 - 6.0                | 5.0 - 6.7                |
|    | W      | —                        | 9.5 - 10.5               | 3.0 - 3.4                | —                        | 0 - 10.5                 |
|    | Ta     | 4.0 - 4.5                | 2.8 - 3.3                | 3.9 - 4.3                | —                        | 0 - 4.5                  |
|    | Mo     | 5.75 - 6.25              | 0.5 - 0.8                | 1.75 - 2.25              | 2.0 - 4.0                | 0.5 - 6.25               |
| 10 | Co     | 9.5 - 10.5               | 9 - 11                   | —                        | 13 - 17                  | 0 - 17.0                 |
|    | Ti     | 0.8 - 1.2                | 0.9 - 1.2                | —                        | 4.5 - 5.0                | 0 - 5.0                  |
|    | Cb(Nb) | —                        | —                        | —                        | —                        | —                        |
|    | Re     | —                        | —                        | —                        | —                        | —                        |
|    | C      | 0.08 - 0.13              | 0.13 - 0.17              | 0.08 - 0.13              | 0.15 - 0.20              | 0.08 - 0.20              |
| 15 | B      | 0.01 - 0.02              | 0.01 - 0.02              | 0.004 - 0.01             | 0.01 - 0.02              | 0.003 - 0.020            |
|    | Zr     | 0.03 - 0.13              | 0.03 - 0.08              | 0.25 - 0.35              | 0.03 - 0.09              | 0.03 - 0.35              |
|    | Y      | —                        | —                        | —                        | —                        | 0.02 - 0.16              |
|    | Hf     | 1.05 - 1.2               | 1.2 - 1.6                | 1.05 - 1.25              | —                        | 1.05 - 1.6               |
|    | Ni     | essentially<br>remainder | essentially<br>remainder | essentially<br>remainder | essentially<br>remainder | essentially<br>remainder |
| 20 |        |                          |                          |                          |                          |                          |

In the nickel-based alloys of the present invention, certain elements that are present either as impurities or minor additions are preferably controlled to be no more than: 0.56% silicon, 0.12% manganese, 0.015% phosphorus, 0.015% sulfur, 0.20% iron, 0.10%

copper, 0.0005% lead, 0.00003% bismuth, 0.0001% selenium, 0.00005% tellurium, and 0.00005% thallium. In other more preferred embodiments, the polycrystalline nickel-based alloys of the present invention described above, comprise 0.13 - 0.17% carbon, 0.01 - 0.15% zirconium, 0.02 - 0.16% yttrium, 0.9 - 1.9% hafnium and 0.003 - 0.010% boron. In a still more preferred embodiment, nickel-based alloys of the present invention comprise about 1.4 weight % hafnium, about 0.005 weight % boron, about 0.15% carbon, about 0.07 weight % zirconium, and about 0.10 weight % yttrium.

In another preferred embodiment, a protective coating is applied to the surface of the build-up repair alloy which has been applied to the substrate alloy. The protective coating layer may be applied by conventional processes. In a preferred embodiment, the protective coating layer is an aluminide-based coating as described in U.S. Patent Nos. 4,132,816; 4,148,275; 4,585,481; 4,897,315; 4,910,092; 4,933,239; and reissue 32,121. In some embodiments, the heat treatment of the protective coating may obviate the need for diffusion and/or stress relief heat treatment of the repair alloy after application to the substrate.

In order to achieve the best thermal match between the substrate alloy and repair alloy, it is desirable to tailor the composition of the repair alloy to the substrate on which the alloy is to be applied. However, in some situations, economic considerations favor use of

a nickel-based alloy of the present invention for build-up applications on nickel-based substrates having a variety of compositions.

5 The methods and alloys of the present invention are useful for build-up applications on alloy substrates, especially nickel-based superalloy substrates, and especially nickel-based single crystal superalloy substrates. Alloys and methods of the present invention can be used to effect repairs of manufacturing defects  
10 as well as defects caused by erosion and wear. Alloys and methods of the present invention are particularly useful for the repair of turbine engine components. They are also useful for other build-up applications that require good durability and oxidation resistance at high  
15 temperature.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of repairing a single crystal alloy by the use of a repair alloy whose composition is substantially similar to that  
20 of the single crystal alloy substrate, and in addition contains at least one grain boundary strengthening element and preferably contains an additional element or elements that increase the oxidation resistance of the polycrystalline repair alloy. The repair alloy can be  
25 applied by methods including: low pressure plasma spray, laser welding, and plasma transferred arc welding. The repair method of the present invention can be applied,

for example, to the leading edge of a turbine blade that has suffered erosion damage. The damaged portion of the blade can be removed by blending and the repair alloy applied to the blended area, followed by recontouring to the original dimensions.

The present invention provides a polycrystalline nickel alloy comprising 0.03 to 1.9 weight % hafnium, 0.003 to 0.32 weight % boron, 0.01 to 0.35 weight % zirconium and 0.02 to 0.16 weight % yttrium. This alloy exhibits good strength and oxidation resistance at high temperatures. In repair applications of the present invention, it is preferred that the alloy contain no more than about 0.010 weight % boron. Larger amounts of boron depress the overall melting point of the alloy system and also result in undesirable oxidation blistering during high temperature exposure.

The nickel alloys of this invention are usually produced by forming ingots of the inventive composition by conventional vacuum induction melting techniques. In preferred embodiments, the alloy is subsequently converted to a powder by gas atomizing or rotary atomizing.

In a preferred embodiment, the powderized repair alloy is applied by a low pressure plasma spray technique. Prior to the plasma spray it is important that the part be thoroughly cleaned and free of dirt, grit, oil, grease or other foreign materials. A coating is then applied by high velocity plasma arc spray of the



repair alloy. Optionally, a powder of the repair alloy may be blended with a relatively small amount of a braze alloy powder. The coated part is then heat treated. If desired, the surface can be hardened by peening with dry  
5 glass or ceramic beads or steel shot. The low pressure plasma spray technique is discussed in U.S. Patent Nos. 4,585,481 and 3,928,026.

In another preferred embodiment, the repair alloy is applied by laser cladding (welding). Laser cladding  
10 can operate using the repair alloy either in powder, preform or wire form. The laser melts the alloy over the area to be repaired to form a coating, which is subsequently annealed. The laser cladding technique is generally discussed in Eboo et al., "Laser Cladding of  
15 Gas Turbine Components", ASME Publication 86-61-298, 1976.

In another preferred embodiment of the present invention, a powdered repair alloy is applied using the plasma transferred arc welding technique. This  
20 technique is described in U.S. Patent No. 4,878,953 (Saltzman et al.).

In one embodiment of the present invention a buildup application of nickel-based repair alloy of the present invention is applied to a single crystal nickel-  
25 based superalloy. Compositions of the substrate alloy and the corresponding repair alloy, in weight %, are set forth in the table below:

TABLE 4

|    |         | single crystal<br>substrate alloy | repair alloy             |
|----|---------|-----------------------------------|--------------------------|
|    | Cr      | 4.75 - 5.25                       | 4.75 - 5.25              |
| 5  | Al      | 5.5 - 5.8                         | 5.5 - 5.8                |
|    | W       | 5.6 - 6.2                         | 5.6 - 6.2                |
|    | Ta      | 8.4 - 9.0                         | 8.4 - 9.0                |
|    | Mo      | 1.7 - 2.1                         | 1.7 - 2.1                |
|    | Co      | 9.5 - 10.5                        | 9.5 - 10.5               |
| 10 | Ti      | --                                | --                       |
|    | Cb (Nb) | --                                | --                       |
|    | Re      | 2.8 - 3.2                         | 2.8 - 3.2                |
|    | C       | 0.050                             | 0.05 - 0.17              |
|    | B       | 0.0030                            | 0.003 - 0.32             |
| 15 | Zr      | 0.0075                            | 0.007 - 0.15             |
|    | Y       | --                                | 0.02 - 0.16              |
|    | Hf      | 0.05 - 0.15                       | 0.05 - 1.9               |
|    | Ni      | essentially<br>remainder          | essentially<br>remainder |

20 Preferably the presence of various additional elements, either as minor additions or as impurities, is limited in the substrate alloy and the repair alloy to the following limits, in weight percent: 0.12% silicon (in less preferred embodiments up to 0.56% silicon in

25 the repair alloy), 0.12% manganese, 0.015% phosphorus, 0.015% sulfur, 0.20% iron, 0.10% copper, 0.0005% lead, 0.00003% bismuth, 0.0001% selenium, 0.00005% tellurium,

and 0.00005% thallium. In more preferred embodiments, the repair alloy contains about: 0.15% carbon, 0.005% boron, 0.07% zirconium, 0.10% yttrium, and 1.4% hafnium.

5 Burner Rig Testing at 1204°C (2200°F) on a variety of repair alloys and coatings was performed. The repair alloys were applied to a divot machined on the surface of nickel-based single crystal superalloy rods. Testing conditions were 1204°C (2200°F) for 375 cycles of 57 minutes hot and 3 minutes forced air cool (FAC) in each cycle. Burner Rig Testing (see Table 5) demonstrated that the build-up repair method of the present invention and an alloy of the present invention (see reference to test bars 2 and 3 on Table 5) are effective in the repair of a damaged single crystal substrate alloy and are superior when compared with other repair methods and alloys.

Visual inspection of the single crystal test specimens following burner rig oxidation testing for 375 cycles at 1204°C (2200°F) was completed. A focused inspection of the repaired regions on the hot side (exposed to flame) of the specimens (bars 2 and 3) showed minimal oxidation erosion or blistering in comparison to the baseline specimen (bar 1). The best indication of good oxidation performance is displayed in samples (such as test bars 2 and 3) that form adherent surface oxidation layers that are typically dull gray in surface appearance. Examples of unacceptably high

oxidation erosion and blistering were displayed on repaired regions of test bars 4 and 5.

Burner Rig Testing: Test Bar Preparation

5 All of the test bars were composed of the same nickel-based superalloy described in the preferred embodiment of U.S. Patent No. 4,719,080. The baseline result was established by test bar 1 which consisted only of the substrate alloy coated with an aluminide alloy as described in U.S. Patent Nos. 4,132,816 and 10 4,148,275.

In test bars 2-8, a .76 mm (0.030 inch) deep divot was blended into each bar. The surface of the divot was cleaned by blasting with fine alumina. Except for test bars 6 and 8, a repair alloy was applied into each 15 depression and the bar was recontoured to the initial diameter of the test bar. The test bars were then coated with a protective coating. All of the protective coatings were diffused at a temperature of about 1121°C (2050°F).

20 Test bar 2 was repaired utilizing a repair alloy having the composition, in weight percent:

|           |       |
|-----------|-------|
| Aluminum  | 5.73  |
| Boron     | 0.021 |
| Carbon    | 0.15  |
| 25 Cobalt | 9.93  |
| Chromium  | 4.99  |
| Copper    | <1.10 |

|    |            |          |
|----|------------|----------|
|    | Iron       | <0.20    |
|    | Hafnium    | 1.21     |
|    | Molybdenum | 1.92     |
|    | Manganese  | <0.12    |
| 5  | Oxygen     | 0.0170   |
|    | Phosphorus | <0.015   |
|    | Sulfur     | <0.015   |
|    | Silicon    | <0.12    |
|    | Tantalum   | 7.89     |
| 10 | Lead       | <0.0005  |
|    | Tungsten   | 6.19     |
|    | Yttrium    | 0.07     |
|    | Zirconium  | 0.090    |
|    | Rhenium    | 3.09     |
| 15 | Selenium   | <0.0001  |
|    | Bismuth    | <0.00003 |
|    | Nickel     | balance  |

20 This repair alloy was blended with a nickel-based braze alloy containing 4.5 weight % silicon and 3.0 weight % boron. The alloys were mixed in a ratio of nine parts repair alloy to one part braze alloy. The mixture was applied to the substrate by low pressure plasma spray. The repair test bar was then coated as described for test bar 1.

25 Test bar 3 was repaired as described above for test bar 2, but then coated with an aluminide coating as described in U.S. Patent Nos. 3,102,044 and 3,544,348.

The repaired test bars were heat treated at 1079°C (1975°F) for 4 hours in a protective atmosphere and cooled to below 427°C (800°F) at 4°C (40°F)/minute or faster.

5        Test bar 4 was repaired using powder fed plasma transferred arc welding with an alloy having the nominal composition Co, 20% Cr, 15% Ni, 9.0% W, 4.4% Al, 3.0% Ta, 1.1% Hf, 0.2% Ti, 0.04% Y, 0.35% C. The powder size used was between 100 and 325 mesh size. The repaired  
10      bar was coated with the same coating as test bar 1.

Test bar 5 was repaired using the same alloy and technique and test bar 4. The repair test bar was coated using the same coating as test bar 3.

15       Test bar 6 was not repaired and was coated with a 5.1 x 10<sup>-5</sup> meter (0.002 inch) - 7.6 x 10<sup>-5</sup> meter (0.003 inch) aluminide coating by the techniques disclosed in U.S. Patent Nos. 4,585,481; 4,897,315; 4,910,092; 4,933,239; and reissue 32,121.

20       Test bar 7 was repaired using a NiAlY repair alloy and coated with the same coating as test bar 1.

Test bar 8 was not repaired, but was coated with the aluminide coating of test bar 1.

25       Although the invention has been described in conjunction with specific embodiments, many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the

alternatives and variations that fall within the spirit and scope of the appended claims.

Table 5: Burner Rig Testing<sup>1</sup>

|    | Test Bar               | Repair Alloy                              | Protective Coating |
|----|------------------------|---|--------------------|
|    | 1. Baseline (no blend) | None                                      | A2                 |
| 5  | 2. LPPS - applied      | 90% repair alloy<br>10% braze alloy       | A                  |
|    | 3. LPPS - applied      | 90% grain-strengthened<br>10% braze alloy | B3                 |
|    | 4. PTA - applied       | Co superalloy                             | A                  |
|    | 5. PTA - applied       | Co superalloy                             | B                  |
| 10 | 6. Blend only          | None                                      | C4                 |
|    | 7. LPPS - applied      | NiAlY                                     | A                  |
|    | 8. Blend only          | None                                      | A                  |

<sup>1</sup>All repair test bars were blended .76 mm (0.030 inch) deep, repaired (except bars 1, 6 and 8), recontoured, coated, and burner rig tested at 1204°C (2200°F) for 375 cycles.

<sup>2</sup>A - coating applied as described in U.S. Patent Nos. 4,132,816 and 4,148,275.

<sup>3</sup>B - coating applied as described in U.S. Patent Nos. 3,102,044 and 3,544,348.

<sup>4</sup>C - coating applied as described in U.S. Patent Nos. 4,585,481; 4,897,315; 4,910,092; 4,933,239; and reissue 32,121.



## WE CLAIM:

1. A polycrystalline nickel-based alloy comprising  
0.03 to 2.5 weight % hafnium, 0.003 to 0.32 weight %  
boron, 0.07 to 0.35 weight % zirconium, and 0.02 to 0.16  
5 weight % yttrium.
2. The alloy of claim 1 having 0.9 - 1.9 weight %  
hafnium, 0.003- 0.010 weight % boron, 0.01 - 0.15 weight  
% zirconium, and 0.02 - 0.16 weight % yttrium.
3. The alloy of claim 1 consisting essentially of the  
10 following elements, in weight percent:
- |    |            |               |
|----|------------|---------------|
|    | chromium   | 4.75 - 10.5   |
|    | aluminum   | 4.75 - 5.8    |
|    | tantalum   | 8.4 - 12.25   |
|    | tungsten   | 3.75 - 6.2    |
| 15 | molybdenum | 0 - 2.1       |
|    | cobalt     | 4.5 - 10.5    |
|    | titanium   | 0 - 1.75      |
|    | rhenium    | 2.8 - 3.2     |
|    | carbon     | 0.05 - 0.17   |
| 20 | boron      | 0.003 - 0.320 |
|    | zirconium  | 0.007 - 0.15  |
|    | yttrium    | 0.02 - 0.16   |
|    | hafnium    | 0.03 - 1.9    |
|    | nickel     | remainder.    |

4. The alloy of claim 3 wherein the following elements are controlled to comprise no more than the following amounts, in weight percent: 0.56% silicon, 0.12% manganese, 0.015% phosphorus, 0.015% sulfur, 0.2.% iron, 0.10% copper, 0.0005% lead, 0.00003% bismuth, 0.0001% selenium, 0.00005% tellurium, and 0.00005% thallium.

5. The alloy of claim 1 wherein the following elements are controlled to comprise no more than the following amounts, in weight percent: 0.56% silicon, 0.12% manganese, 0.015% phosphorus, 0.015% sulfur, 0.2.% iron, 0.10% copper, 0.0005% lead, 0.00003% bismuth, 0.0001% selenium, 0.00005% tellurium, and 0.00005% thallium.

6. The alloy of claim 1 consisting essentially of the following elements, in weight percent:

|    |            |               |
|----|------------|---------------|
| 15 | chromium   | 4.75 - 5.25   |
|    | aluminum   | 5.5 - 5.8     |
|    | tungsten   | 5.6 - 6.2     |
|    | tantalum   | 8.4 - 9.0     |
|    | molybdenum | 1.7 - 2.1     |
| 20 | cobalt     | 9.5 - 10.5    |
|    | titanium   | 0 - 1.75      |
|    | rhenium    | 2.8 - 3.2     |
|    | carbon     | 0.13 - 0.17   |
|    | boron      | 0.003 - 0.010 |
| 25 | zirconium  | 0.01 - 0.15   |
|    | yttrium    | 0.02 - 0.16   |

|         |           |
|---------|-----------|
| hafnium | 0.9 - 1.9 |
| nickel  | remainder |

7. The alloy of claim 4 comprising less than 0.12 weight silicon and further comprising in weight percent, about:

|           |        |
|-----------|--------|
| carbon    | 0.15%  |
| zirconium | 0.07%  |
| boron     | 0.005% |
| yttrium   | 0.10%  |
| hafnium   | 1.4%.  |

8. The alloy of claim 1 consisting essentially of the following elements, in weight percent:

|            |               |
|------------|---------------|
| chromium   | 6.0 - 10.0    |
| aluminum   | 4.75 - 6.1    |
| tungsten   | 6.0 - 12.5    |
| tantalum   | 0 - 4.25      |
| molybdenum | 0 - 1.9       |
| cobalt     | 9.25 - 13.0   |
| titanium   | 0 - 2.25      |
| niobium    | 0 - 1.25      |
| rhenium    | 0 - 3.25      |
| carbon     | 0.08 - 0.16   |
| boron      | 0.003 - 0.020 |
| zirconium  | 0.04 - 0.12   |
| yttrium    | 0.02 - 0.16   |
| hafnium    | 1.0 - 2.5     |

nickel                      remainder.

9. The alloy of claim 1 consisting essentially of the following elements, in weight percent:

|    |            |               |
|----|------------|---------------|
|    | chromium   | 7.5 - 11.0    |
| 5  | aluminum   | 5.0 - 6.7     |
|    | tungsten   | 0 - 10.5      |
|    | tantalum   | 0 - 4.5       |
|    | molybdenum | 0.5 - 6.25    |
|    | cobalt     | 0 - 17.0      |
| 10 | titanium   | 0 - 5.0       |
|    | carbon     | 0.08 - 0.20   |
|    | boron      | 0.003 - 0.020 |
|    | zirconium  | 0.03 - 0.35   |
|    | yttrium    | 0.02 - 0.16   |
| 15 | hafnium    | 1.05 - 1.6    |
|    | nickel     | remainder.    |

10. The alloy of claim 1 exhibiting good oxidation resistance at 2200°F.

20 11. A use of the alloy of claim 1 to repair a substrate alloy.

12. A use of the alloy of claim 3 to repair a single crystal nickel-based superalloy substrate.

13. The use of claim 12 wherein said single crystal nickel-based superalloy substrate is a component of a turbine engine.

5 14. A method of creating a build-up alloy application on a nickel-based superalloy substrate comprising the application of a nickel-based repair alloy onto said nickel-based superalloy substrate; wherein said nickel-based repair alloy comprises 0.03 to 2.5 weight % hafnium, 0.003 to 0.32 weight % boron, 0.007 to 0.35  
10 weight % zirconium, and 0.02 to 0.16 weight % yttrium.

15. The method of claim 14 wherein said repair alloy is applied to said substrate by a process selected from the group consisting of low pressure plasma spray, laser welding and plasma arc welding.

15 16. The method of claim 15 further comprising blending a portion of the surface of said substrate to create a blended area, and, subsequent to said blending, applying said repair alloy onto said blended area.

20 17. The method of claim 15 further comprising in a step subsequent to said application of said repair alloy, the application of a protective coating over said repair alloy.

18. The method of claim 14, wherein said superalloy substrate is a single crystal superalloy substrate, and further wherein said repair alloy consists essentially of the following elements, in weight percent:

|    |            |               |
|----|------------|---------------|
| 5  | chromium   | 4.75 - 10.5   |
|    | aluminum   | 4.75 - 5.8    |
|    | tungsten   | 3.75 - 6.2    |
|    | molybdenum | 0 - 2.1       |
|    | cobalt     | 4.5 - 10.5    |
| 10 | titanium   | 0 - 1.75      |
|    | rhenium    | 2.8 - 3.2     |
|    | carbon     | 0.05 - 0.17   |
|    | boron      | 0.003 - 0.320 |
|    | zirconium  | 0.007 - 0.15  |
| 15 | yttrium    | 0.02 - 0.16   |
|    | hafnium    | 0.03 - 1.9    |
|    | nickel     | remainder     |

19. The method of claim 14, wherein said superalloy substrate is a directionally solidified superalloy substrate, and further wherein said repair alloy consists essentially of the following elements, in weight percent:

|    |          |            |
|----|----------|------------|
|    | chromium | 6.0 - 10.0 |
|    | aluminum | 4.75 - 6.1 |
| 25 | tungsten | 6.0 - 12.5 |
|    | tantalum | 0 - 4.25   |

|    |            |                        |   |       |
|----|------------|------------------------|---|-------|
|    | molybdenum | 0                      | - | 1.9   |
|    | cobalt     | 9.25                   | - | 13.0  |
|    | titanium   | 0                      | - | 2.25  |
|    | niobium    | 0                      | - | 1.25  |
| 5  | rhenium    | 0                      | - | 3.25  |
|    | carbon     | 0.08                   | - | 0.16  |
|    | boron      | 0.003                  | - | 0.020 |
|    | zirconium  | 0.04                   | - | 0.12  |
|    | yttrium    | 0.02                   | - | 0.16  |
| 10 | hafnium    | 1.0                    | - | 2.5   |
|    | nickel     | essentially remainder. |   |       |

20. The method of claim 14 wherein said superalloy substrate in an equiaxed superalloy substrate, and further wherein said repair alloy consists essentially of the following elements, in weight percent:

|    |            |       |   |       |
|----|------------|-------|---|-------|
|    | chromium   | 7.5   | - | 11.0  |
|    | aluminum   | 5     | - | 6.7   |
|    | tungsten   | 0     | - | 10.5  |
|    | tantalum   | 0     | - | 4.5   |
| 20 | molybdenum | 0.5   | - | 6.25  |
|    | cobalt     | 0     | - | 17.0  |
|    | titanium   | 0     | - | 5.0   |
|    | carbon     | 0.08  | - | 0.20  |
|    | boron      | 0.003 | - | 0.020 |
| 25 | zirconium  | 0.03  | - | 0.35  |
|    | yttrium    | 0.02  | - | 0.16  |

|         |            |
|---------|------------|
| hafnium | 1.05 - 1.6 |
| nickel  | remainder. |

21. The method of claim 15 wherein, in said repair alloy the alloy of claim 3 wherein the following  
5 elements are controlled to comprise no more than the following amounts, in weight percent: 0.56% silicon, 0.12% manganese, 0.015% phosphorus, 0.015% sulfur, 0.2.% iron, 0.10% copper, 0.0005% lead, 0.00003% bismuth, 0.0001% selenium, 0.00005% tellurium, and 0.00005%  
10 thallium.

22. The method of claim 14 wherein said repair alloy comprises 0.9 to 1.9 weight % hafnium, 0.003 to 0.010 weight % boron, 0.01 to 0.15 weight % zirconium, 0.02 to 0.16 weight % yttrium, and 0 to 0.12 weight % silicon.

15 23. A substrate repaired by the method of claim 15.

24. A method of creating a build-up alloy application on a single crystal superalloy substrate comprising the steps of:

20 making a repair alloy that is composed of substantially the same elements in substantially the same proportions as in said single crystal superalloy substrate except that said repair alloy additionally comprises at least one grain boundary strengthener element; and applying said repair alloy to said single



crystal superalloy substrate by a low substrate heat input buildup process.

25. The method of claim 24 wherein said superalloy substrate is a single crystal nickel-based superalloy, and said repair alloy is a nickel-based alloy comprising 0.9 to 1.9 weight % hafnium, 0.003 to 0.010 weight % boron, 0.01 to 0.15 weight % zirconium, and 0.02 to 0.16 weight % yttrium.

26. The method of claim 25 wherein said repair alloy is not mixed with a lower melting alloy, and is applied to said single crystal substrate by a method selected from the group consisting of low pressure plasma spray, laser welding and plasma arc welding.

27. The method of claim 25 wherein said repair alloy consists essentially of the following elements, in weight percent:

|    |            |      |         |
|----|------------|------|---------|
|    | carbon     | 0.13 | 0.17    |
|    | manganese  | --   | 0.12    |
|    | silicon    | --   | 0.12    |
| 20 | phosphorus | --   | 0.015   |
|    | sulfur     | --   | 0.015   |
|    | chromium   | 4.75 | - 5.25  |
|    | cobalt     | 9.50 | - 10.50 |
|    | molybdenum | 1.70 | - 2.10  |
| 25 | tungsten   | 5.60 | - 6.20  |

|    |           |       |   |                   |
|----|-----------|-------|---|-------------------|
|    | rhenum    | 2.80  | - | 3.20              |
|    | tantalum  | 7.80  | - | 9.00              |
|    | aluminum  | 5.18  | - | 5.78              |
|    | yttrium   | 0.02  | - | 0.16              |
| 5  | hafnium   | 0.9   | - | 1.9               |
|    | boron     | 0.003 | - | 0.010             |
|    | iron      | --    |   | 0.20              |
|    | copper    | --    |   | 0.10              |
|    | zirconium | 0.01  | - | 0.15              |
| 10 | lead      | --    |   | 0.0005 (5 ppm)    |
|    | bismuth   | --    | - | 0.00003 (0.3 ppm) |
|    | selenium  | --    |   | 0.0001 (1 ppm)    |
|    | tellurium | --    |   | 0.00005 (0.5 ppm) |
|    | thallium  | --    |   | 0.00005 (0.5 ppm) |
| 15 | nickel    |       |   | remainder.        |

28. The method of claim 26 further comprising a step of applying a protective coating following said step of applying said repair alloy.

29. A substrate repaired by the process of claim 25.

20 30. A repair alloy suitable for the repair of a single crystal superalloy substrate wherein said repair alloy is composed of substantially the same elements in substantially the same proportion as in said single crystal superalloy substrate except that said repair alloy additionally comprises at least one grain boundary strengthener element; and wherein the levels of

25

additional grain boundary strengtheners in said repair alloy are insufficient to substantially reduce the bulk melting point of said repair alloy.

5 31. The repair alloy of claim 30 additionally comprising at least one element that enhances oxidation resistance.

10 32. The repair alloy of claim 31 wherein said substance is a nickel-based superalloy and said repair alloy is a nickel-based alloy and further, wherein said grain boundary strengtheners comprise at least two elements selected from the group consisting of zirconium, hafnium, and boron.

15 33. The repair alloy of claim 32, wherein said repair alloy comprises 0.9 to 1.9 weight % hafnium, 0.003 to 0.010 weight % boron, 0.01 to 0.15 weight % zirconium, and 0.02 to 0.16 weight % yttrium.

34. The repair alloy of claim 33 consisting essentially of the following elements, in weight percent:

|    |            |       |                     |
|----|------------|-------|---------------------|
|    | carbon     | 0.13  | 0.17                |
|    | manganese  | --    | 0.12                |
| 5  | silicon    | --    | 0.12                |
|    | phosphorus | --    | 0.015               |
|    | sulfur     | --    | 0.015               |
|    | chromium   | 4.75  | - 5.25              |
|    | cobalt     | 9.50  | - 10.50             |
| 10 | molybdenum | 1.70  | - 2.10              |
|    | tungsten   | 5.60  | - 6.20              |
|    | rhenium    | 2.80  | - 3.20              |
|    | tantalum   | 7.80  | - 9.00              |
|    | aluminum   | 5.18  | - 5.78              |
| 15 | yttrium    | 0.02  | - 0.16              |
|    | hafnium    | 0.9   | - 1.9               |
|    | boron      | 0.003 | - 0.010             |
|    | iron       | --    | 0.20                |
|    | copper     | --    | 0.10                |
| 20 | zirconium  | 0.01  | - 0.15              |
|    | lead       | --    | 0.0005 (5 ppm)      |
|    | bismuth    | --    | - 0.00003 (0.3 ppm) |
|    | selenium   | --    | - 0.0001 (1 ppm)    |
|    | tellurium  | --    | - 0.00005 (0.5 ppm) |
| 25 | thallium   | --    | - 0.00005 (0.5 ppm) |
|    | nickel     |       | remainder.          |

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/08008

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C22C19/05 B23K35/30 //B23P6/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C22C B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X          | EP,A,0 362 661 (GEN ELECTRIC) 11 April 1990<br>see claim 1<br>---  | 1,2,<br>30-33         |
| X          | EP,A,0 194 391 (GEN ELECTRIC) 17 September 1986<br>see page 4, line 19 - line 25<br>see page 9, line 26 - line 35<br>see page 5, line 2 - line 7; table 3<br>--- | 24                    |
| A          | WO,A,92 03241 (LIBURDI ENGINEERING<br>;LIBURDI JOSEPH (CA); LOWDEN PAUL (CA);<br>ELLISO) 5 March 1992<br>---<br>-/--   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

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